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JC20 Rec'd PCT/PTO 29 JUN 2009EXPANDABLE ANODES FOR CHLOR-ALKALI DIAPHRAGM CELLS

Chlor-alkali electrolysis is the electrolytic process of widest industrial interest together with the production of aluminium from molten salts.

Chlor-alkali electrolysis is presently carried out making use of three types of technology, namely the mercury cathode, the diaphragm and the ion-exchange membrane one. The membrane technology is the latest of the three and is invariably employed for the construction of new plants and the retrofitting of old plants whose cells have reached the end of service life. The remaining two are technologies developed in particular during the '40es and '50es and are still the basis of plants accounting for about 70% of the world production. While mercury cathode electrolysis is destined to be sooner or later abandoned, not primarily for technical reasons but rather for the by now consolidated opposition of the public opinion to any industrial process that might, even only potentially, introduce heavy metals in the environment, the diaphragm electrolysis maintains a remarkable validity in view of the technical improvements which have taken place in the years, that allowed to sensibly lower the energy consumption and to achieve new types of diaphragm free of asbestos, which was originally its main component. These new types of diaphragm, whose use is progressively spreading in the industrial plants, are made of a complex mixture of inorganic particles and fibres, for instance zirconium oxide, stabilised by a chemically inert polymeric binder such as for example polytetrafluoroethylene (PTFE) with formation of a porous film characterised by better structural stability and better mechanical properties than those typical of the conventional asbestos-based diaphragms.

Among the other technical improvements which have been brought in the diaphragm chlor-alkali electrolysis technology, particularly relevant are the modifications to the internal design of the cells and in particular of the anodes which have permitted to decrease the operating voltage, and therefore the electric energy consumption which is a direct function thereof, to a remarkable extent.

As regards the anodes, graphite, that was the original construction material, has been nearly totally replaced by titanium coated with an electrocatalytic film made

of mixtures of platinum group metal oxides. The machinability and weldability of the new material, which is routinely provided in form of sheet, expanded sheet and perforated sheet, allowed adopting a new geometric shape known as "box" which produced a remarkable cell voltage reduction compared to that typical of the graphite anodes. With the "box" anodes, a sensible gap however exists, indicatively of 5 millimetres, between the surface of the same anodes and the surface of the diaphragms: this gap, necessary to permit the introduction of the anodes into the cell body without damaging the diaphragm, entails an energy consumption due to the ohmic drop generated by the passage of electric current through the brine present in the gap itself. To minimise this energy consumption, the "box" anodes are generally replaced by the so called expandable anodes, nowadays widely used, in which the two main surfaces facing the diaphragm are connected to the current collecting stem through a pair of flexible titanium sheets: in this way the two surfaces result movable and may be retained by means of appropriate constraint elements in order to permit the installation of the anode into the cell body without damaging the diaphragm. Once the installation is completed, the constraint elements are extracted and the movable sheets are left free to expand under the action of the connecting flexible sheets. The movable surfaces of the expandable anode should ideally contact the diaphragm surfaces suppressing the gap of about 5 millimetres which is typical, as mentioned above, of the "box" anodes, eliminating thereby the relevant ohmic drop in the brine and the associated electric energy consumption. Actually, the pressure exerted by the flexible sheets tends to exhaust before the anode surfaces come in contact with the diaphragm surface. This is due both to a certain relaxation experienced by the flexible sheets during the phase of holding in the retained position, and to the need of limiting the pressure exerted by the same flexible sheets in the retained position to allow an easy extraction of the constraint elements. The result of this situation is that the gap between the anode and diaphragm surfaces is certainly decreased with respect to the typical situation of the "box" anodes, but it's not completely suppressed, with a consequent residue of electric energy consumption associated to the remnant of a partial ohmic drop. Moreover it is not possible to produce anodes wherein the two flexible sheets connecting the movable surfaces to the

current collecting stem are exactly equivalent: actually, either due to differences of thickness or mechanical characteristics or to manufacturing, albeit within the range of the design tolerances, it happens that the expansion is not uniform, giving rise to a difference of alignment of the anode surfaces with respect to the diaphragm surfaces and a lack of parallelism between the two. This situation implies a lack of uniformity in the current distribution inside each cell with increase of the operating voltage and decrease of efficiency.

In patent US 5,534,122 an improved expandable anode structure is disclosed, wherein after the installation in the cell and after the extraction of the constraint elements the anode expansion is completed by means of the introduction of appropriate forcing elastic elements (shown in figure 3 of the cited patent). In this way the anode and diaphragm surfaces are brought in complete contact and in fact a decrease in the cell voltage compared to that typical of the conventional expandable anodes is generally observed. The practical experience deriving from the extended use in time of the forcing elements of US 5,534,122 has nevertheless demonstrated that damages to the diaphragms may be produced, probably associated to excessively high levels of compression. This inconvenience derives from the fact that the allowable gap for the action of the forcing elements is necessarily the one defined by the distance between the opposed diaphragm surfaces, known to those skilled in the art as cathode finger gap. This gap is not precisely defined as it may vary to a substantial extent under the effect of construction tolerances and of certain deformations which may occur during the diaphragm deposition, in particular during the two steps of deposition by vacuum suction and of thermal stabilisation of the deposited diaphragm. It follows that the span of the forcing elastic elements is necessarily variable from cell to cell and depending from the position inside each cell. Since the span of the forcing elastic elements is inversely proportional to the exerted pressure, it follows that in the points where the cathode finger gap is lower, a higher compression is localised on the diaphragm, which in the most serious of cases can bring to damages over time as in fact has sometimes been observed in the industrial practice.

OBJECTS OF THE INVENTION

The scope of the present invention is to overcome the inconveniences associated with the use of the forcing elastic elements known in the art allowing to obtain a complete expansion of the movable anode surfaces while guaranteeing a homogeneous and freely adjustable diaphragm compression, particularly as a function of the diaphragm quality and of the mechanic characteristics thereof.

Thus in a first aspect the present invention provides the use of forcing elastic elements installed inside expandable type anodes, wherein such elements are characterised by having an adjustable span.

In a second aspect of the invention the span of the forcing elastic elements is externally adjustable after the installation of said expandable anodes in the electrolysis cells.

In a third aspect the outside span adjustment of the elastic elements of the invention is carried out with an extractable tool.

In a fourth aspect said extractable tool is characterised by high torque resistance.

In a fifth aspect said high torque resistance extractable tool is made of a low-alloy steel in a quenched and tempered state.

In a sixth aspect the forcing elastic element of the invention also acts as a constraint element capable of holding the expandable anode in a restrained condition during the installation in the cell, so as to prevent damaging of the diaphragm.

In a seventh aspect the forcing elastic element of the invention is suitable as well for being introduced in expandable anodes constructed according to the indications of the prior art and previously operated.

In an eight aspect the forcing elastic element of the invention consists of a sheet having a U-shaped profile and provided with at least one externally operated span adjusting device.

In a ninth aspect the externally operated span adjusting device comprises a collar fastening said forcing elastic element through appropriate openings made in said element and which is operated by a suitable gear.

In a tenth aspect said gear is rotated by means of the extractable tool.

In a further aspect the externally operated span adjusting device consists, in a second embodiment, of a threaded shaft or of a pair of threaded shafts operated

by means of an appropriate lever.

In a final aspect the forcing elastic element consisting of the U-shaped sheet provided with span adjusting device is also provided with fins engaging the connecting flexible sheets in the restrained position before the installation.

DETAILED DESCRIPTION OF THE INVENTION.

The invention is disclosed below making reference to the following figures:

- figure 1: chlor-alkali electrolysis cell provided with fingers whereon the diaphragm is deposited and provided with anodes fastened to the conductive base and intercalated to the fingers
- figure 2: "box"-type anode according to the prior art
- figure 3: expandable-type anode provided with constraint elements according to the prior art
- figure 4: expandable-type anode provided with forcing elastic elements according to the prior art
- figure 5: expandable-type anode provided with adjustable forcing elastic elements according to a first embodiment of the invention and comprising a collar
- figure 6: detail of the adjustable forcing elastic element according to the first embodiment of the invention of figure 5 in which the gear operating the collar is shown
- figure 7: expandable-type anode provided with the adjustable forcing elastic elements according to the first embodiment of the invention of figure 5 and connected to the tool for external adjustment
- figure 8: expandable-type anode provided with adjustable forcing elastic elements according to a further embodiment of the invention
- figure 9: top-view of the adjustable forcing elastic element according to the further embodiment of figure 8 in which the mechanism based on a pair of threaded shafts adjusting the span of the edges of the elastic forcing element is shown
- figure 10: section of the expandable-type anode provided with adjustable forcing elastic elements of figure 8 wherein a different rotation point of the

adjustment mechanism is shown

Figures 1, 2, 3 and 4 represent schemes of a diaphragm chlor-alkali electrolysis cell and of anodes according to the prior art whose brief description is considered to be useful for a better understanding of the finding of the invention.

In particular, as regards the cell of figure 1, the main component parts result to be the fingers (1) made of a carbon steel mesh longitudinally welded so as to constitute a cylinder which is then squeezed to form a rather flat box whereof the figure shows the cross-section and whereon a porous diaphragm is deposited, the conductive base (2) whereto the anodes (3) are secured by bolts (4), intercalated to the fingers (1) in the relevant gap (11), the cover (5) provided with nozzles (6) and (7) respectively for the brine inlet and for the product chlorine outlet, nozzles (8) and (9) respectively for the discharge of hydrogen and for the outlet of the liquid containing the product caustic soda mixed with the exhaust brine.

During operation, the cell wall (10), whereto the fingers (1) are secured, and the conductive base (2) are respectively connected to the negative polarity and to the positive polarity of a rectifier.

The cell assemblage comprises the following steps: diaphragm deposition on the fingers (1) and the wall (10) with subsequent stabilising thermal treatment, securing of the anodes (3) to the conductive base (2), positioning of the cell body consisting of the fingers (1) and wall (10) on the conductive base (2) so that the fingers and the anodes result reciprocally intercalated, as shown in the figure. This latter passage is very critical since it must be avoided that the anodes (3) graze against the diaphragm deposited on the fingers (1) damaging the same.

The anodes (3), employed to replace the old anodes consisting of graphite plates, may be substantially of two types, "box" or expandable.

The structure of the "box" anode is shown in figure 2, wherein (12) indicates a conductive current collecting stem generally of copper-lined titanium, (13) a titanium mesh, for instance an expanded sheet, coated with an electrocatalytic film for chlorine evolution and shaped so as to form a rigid box of essentially flat section simulating the perimeter of the old graphite plate anodes, (14) an optional second titanium fine mesh also provided with an electrocatalytic film and directed to ensure a better cell voltage, (15) a rigid titanium sheet which permits to anchor

the mesh (13) to the conductive stem (12) and to distribute the electrolysis current. Recalling the above mentioned way according to which the diaphragm cells are assembled, it is clear that the width (16) of the "box" anode must be substantially lower than the gap (11) to avoid damaging the diaphragm while positioning the cell body on the conductive base (2). It follows that in operation the "box" anode surface is necessarily spaced apart from the facing diaphragm-bearing finger surfaces. Such spacing is in general of about 5 millimetres and causes an increase in the cell voltage and in the associated energy consumption.

To avoid this inconvenience the "box" anodes are in general replaced by the more recent expandable anodes, whose structure is sketched in figure 3, wherein the same numerals identifying the common parts with the "box" anodes have been maintained.

It can be noticed in particular that the mesh (13) doesn't form a rigid box anymore, being instead subdivided into two independent movable surfaces, (13A) and (13B), each secured to the conducting stem (12) by the sheets (15) which are elastic, contrarily to the corresponding rigid sheets of the "box" anodes. The anode is provided with a pair of constraint elements (17) that are installed inside the same anode so as to engage the ends of the elastic sheets (15). The constraint elements hold therefore the anode in the restrained position so that they substantially reduce the width (16) allowing a safe assemblage of the cell body on the conductive base. Once completed the assemblage, the constraint elements (17) are extracted releasing the ends of the elastic sheets (15), which can now freely expand hence pushing the surfaces of (13A) and (13B) toward the relevant facing diaphragm-bearing finger surfaces. The scope of this construction is to bring the anode and finger surfaces in direct contact so as to eliminate the voltage penalty that, as seen above, characterises the "box" anodes. The industrial practice has actually shown that this ideal alignment is not achieved: the reasons for this situation are of various kinds, in particular being associated to a certain relaxation undergone by the elastic sheet material when the anode is held in the restrained position and to the need of keeping within reasonable limits the pressure exerted by the same sheets in the restrained position in order to allow an easy extraction of the constraint elements after the cell assemblage. In any case

what is observed is that surfaces (13A) and (13B) of each anode are normally not in direct contact with the surface of the fingers, wherefrom they are positioned at a more or less reduced, but not null and, more importantly, non symmetrical distance. This lack of symmetry, which causes an irregularity in the electric current distribution, is generated by an inevitable variation in the span of the elastic sheets (15) due to differences of mechanical characteristics and of thickness, even if contained in the fabrication tolerances. From a practical standpoint all this prevents to eliminate completely the voltage penalty characterising the "box" anodes.

Figure 4 illustrates a proposal directed to overcome this problem: in particular it is provided that, after assembling the cell and extracting the constraint elements as occurs for the conventional expandable anodes, elastic forcing elements (18) are inserted in the anode, consisting of strips of elastic titanium sheet having for instance a V or U-shaped profile capable of bringing the surfaces (13A) and (13B) in direct contact with the facing finger surfaces. In the practice a minimisation of the cell voltage is in fact observed due to the abolition of the anode to finger surface gap: with the prolongation of the operating time an increasing diaphragm impairment takes place forcing to put the cells out of order. The impairment is most likely due to the high value that the pressures for forcing the anode surfaces against the finger surfaces may assume. These pressures in fact depend, for a given forcing element type, from the span of the same elements, and the span is in its turn conditioned by the value of the gap between two adjacent fingers, wherein such gap is variable from cell to cell and within each cell depending from the relevant position as a consequence of the construction techniques and of the thermal treatments carried out during the cell construction itself and during the diaphragm stabilisation phase.

In the zones where the gap is lower, the span of the forcing elements is also lower and the pressure exerted on the diaphragm deposited on the fingers is higher.

The present invention is intended to solve the problems of the prior art through the use of externally adjustable forcing elastic elements compatible with the design of conventional expandable anodes. A first embodiment of the invention is presented in the axonometric views of figures 5, 6 and 7, wherein the parts in common with

the previous figures are indicated with the same numerals and wherein (19) represents the adjustable forcing elastic element according to the invention provided with edges (27) and with the mechanism (20) for controlling the span of the same edges, (26) and (28) the fins and the folds of the edges (27) engaging the ends of the elastic sheets (15) and allowing the required contraction thereof during the step of cell assemblage, and their controlled expansion during the step of adjustment to be performed after the assemblage, (21), (22), (23) and (24) the component of the control mechanism (20), (30) and (31) a handle and a shaft which form a preferably extractable tool to be employed for the outside adjustment of the span of edges (27).

In particular, in figure 5 the adjustable forcing elastic elements (19) are shown before the insertion in the expandable anode (3) and in figure 7 after the insertion: as it is observed, in the latter position the edges (27) of the adjustable forcing elastic element engage the ends of the elastic sheets (15) in a dual manner, respectively by means of the insertion of the ends of the sheets (15) in the recess generated by the fins (26) (obtained by making an indentation in the edges (27) and appropriately deforming the material towards the outside) and by means of the insertion of the end of the edges (27) inside the terminal part of the sheets (15). This type of mechanic connection permits both contracting the anode (3) by decreasing the span of edges (27) and expanding the same by drawing the edges away in a controlled fashion. It must be noticed therefore that the adjustable forcing elastic element of the invention allows eliminating the use of the constraint elements (17) of the prior art.

The mechanism for adjusting the span of the edges (27) is shown in detail in figure 6: the heart of the mechanism consists of the collar (21) which, through a slit (25) made on both edges (27), fully encloses the apex thereof having an adequately cylindrical shape so as to optimise the overall elastic behaviour of the forcing element. The run of the collar (21), which varies the diameter thereof whereon the higher or lower span of the edges (27) depends, is determined by the rotation of the gear or pinion (23) housed within the two supports (22) and whose cogs engage the knurls (29) of the collar (21). The gear or pinion (23) is provided with a central hole (24), for instance having hexagonal section as shown in figure 6. To

allow the best regulation, each forcing elastic element is preferably provided with at least two mechanisms (20): when two mechanisms are employed, they are positioned in correspondence of both the upper and the lower part of the forcing elastic element.

The operation of the mechanism (20) is illustrated in figure 7. Once the cell has been assembled with the anodes (3) held in the restrained position by the forcing elastic element (19) whose edges (27) are thus reciprocally drawn near, the tool, consisting of a handle (30) and a shaft (31), of section slightly lower than the section of the hole (24) and of same shape, is introduced into the hole (24) of the upper mechanism (20) and then into the hole (24) of the lower mechanism (20). The tool is then rotated, thereby rotating also the gears or pinions (23) of the two upper and lower mechanisms (20): the rotation of the gears or pinions (23) drives the collar (21) running inside the slits (25). The diameter of the collar increases or decreases depending on the sense of rotation imparted by the adjusting tool hence correspondingly increasing or decreasing the span of the edges (27) under the action of the internal elastic forces of the material. With the illustrated device it is therefore possible to determine the span degree of the edges (27) at will, for instance in the optimal restrained position allowing to carry out the cell assemblage in the most reliable fashion without risks of damaging the diaphragm, and in the expanded position with a span exactly limited to what required for making the anode surfaces (13A) and (13B) coincide with the facing finger surfaces without generating uselessly and dangerously high contact pressures. Some particular types of diaphragm result very sensible to the abrading action of the chlorine bubbles generated on the anode surfaces (13A) and (13B). In these cases it is preferable to avoid the direct contact between anode and diaphragm surfaces, therefore with the device of the invention it is easier to adjust the span of the edges (27) and thus the position of the anode surfaces so as to maintain a predetermined distance, useful to substantially lessen the abrading effect of the chlorine bubbles.

Upon completion of the adjustment procedure, which is clearly different from anode to anode depending on the position inside the cell and from cell to cell, the adjusting tool is extracted. It follows that the adjusting tool is not subject to the

highly corrosive action of the cell fluid processes and therefore, in the choice of the construction material therefor, the mechanic characteristics, in particular the torque resistance, can be privileged: for example the low-alloy heat treatable chromium-nickel-molybdenum steels with an adequate thermal treatment are particularly fit.

It has to be observed that the span adjustment procedure may be repeated over time, for instance during plant maintenance, for example in order to compensate for diaphragm dimensional variations as it may happen with some types after specific operating periods.

The forcing elastic elements which, contrarily to the extractable tool, remain inserted in the anodes with the relevant adjustment mechanisms, are subjected to the severe conditions of aggressiveness typical of chlor-alkali cell operation. In this case, titanium and some alloys thereof result to be the elected material for assembly construction.

Figures 8, 9 and 10 represent a further embodiment of the invention. In particular in figure 8 it is shown an axonometric top-view of an anode (3) inserted between the fingers (1) whereon the diaphragm is deposited: the components in common with the previous figures are designated with the same identifying numerals, moreover (32) indicates the adjustment mechanism of the second embodiment and (33) the adjustment tool consisting of a rigid lever which is fixed in a suitable housing of mechanism (32). The mechanism (32) is described in more detail in figure 9 and comprises two blocks (34) united to the edges (27) of the forcing elastic element, a pair of threaded shafts (35), one with a right and the other with a left thread, whose rotation determines, by means of a more or less deep advancement into a suitable recess inside the blocks (34), a more or less pronounced span of the edges (27) and therefore a higher or lower span (16) of the surfaces (13A) and (13B) of the anodes (3). The free end of the threaded shafts (35) is secured to two plates (36) in their turn fastened to a cylinder (37). The tool (33) is provided with suitable indentations (not shown in the figures) allowing the fixing on the cylinder (37): the tool (33)-cylinder (37)-plate (36) assembly acts as a crank allowing to rotate the threaded shafts (35) thereby effecting a vertical alternate displacing of the tool (33). Figure 9 shows also that

the tool (33) is provided with longitudinal protuberances (38) increasing the rigidity thereof which permit to contain the thickness of the sheet employed to construct the tool (33), as necessary to allow its fixing on the cylinder (37) between the two sheets (36). Again in figure 9 it is shown how the ends of the elastic sheets (15) are inserted in the recess formed by the fins (26) and the folds (28) present on the edges (27) of the flexible forcing elements. To allow a perfectly symmetric regulation in the vertical direction it is preferable that each flexible forcing element be provided with at least two mechanisms (32) placed in correspondence of both the upper and lower part.

For a better understanding of the second embodiment of the finding of the invention figure 10 represents a section of the finger (1)-anode (3)- flexible forcing element with part of the adjusting mechanism evidenced.

As in the case of the first embodiment, also in the second embodiment the tool (33) is preferably extracted after completing the adjustment of the anode span in each cell of the plant and thus, being not subjected to the harsh operating conditions, it may be constructed with materials characterised only by high mechanic characteristics, such as for instance low-alloy steels: it is to be noted that the tool of the latter embodiment is however subjected to moderate mechanic solicitations and that in particular the torque stresses, typical of the former embodiment, are conversely absent.

Also in the second embodiment the forcing elastic elements and the relevant adjusting mechanisms must be of course preferably made of titanium or titanium alloys.

Various modifications of the device of the invention may be devised by experts of the field without however departing from the spirit and the scopes of the invention itself which is intended to be limited only as defined in the appended claims.